PROCEEDINGS

Chemical Engineering Seminar
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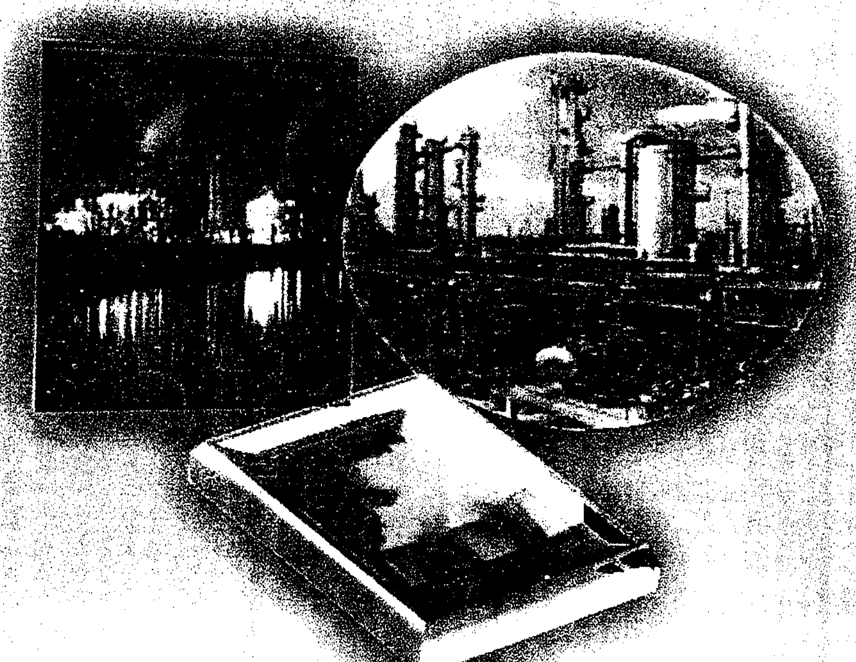
WasteBased Energy and Chemicals



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CRUDE FISH OILS TRANSESTERIFICATION IN AN OSCILLATORY REACTOR

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Abstract

Oscillatory flow mixing provides highly effective mixing in tube reactors by the combination of fluid oscillations and baffle inserts. A continuous process in producing fatty acid methyl esters from crude fish oil by using an oscillatory reactor was discussed in this paper. In this study, the effects of process parameters, including operating temperatures, feeding methanol to crude fish oil ratio, and reaction time, were conducted on a laboratory scale oscillatory flow reactor system. From all variables studied, it seemed that temperature had the highest effect. The results showed that the optimum condition was attained at temperature of 60°C, methanol to crude fish oil ratio of 5:1 (molar), and sodium hydroxide concentration of 1% weight of crude fish oil with conversion of oil bio-diesel was 94.2%; ester numbers was 251.4. Total reaction time in a novel oscillatory reactor was about 12 minutes, which is about 10 times shorter than in typical batch processes. The productivity of the oscillatory reactor is 6 times higher than that of a batch process.

Keywords: *Transesterification, Crude Fish Oil, Oscillatory Reactor, Methyl Esters.*

INTRODUCTION

In principle all edible oils and fats vegetable and animal can be trans-esterified and fatty acids can be esterifies. Among the animal fat sources, crude fish oil is identified as potential biodiesel source and comparing with other sources. The crude fish oil is produced from waste of fish meal and canned fish processing in Muncar, East Java through extraction process. The most common method for producing biodiesel is the one step batch process. Batch processes have suffered several disadvantages compared to continuous processes because batch processes require larger reactor volume. Many long residence time processes are currently performed in batch, as conventional designs of plug flow reactor prove to be impractical due to their high length-to-diameter ratios, which lead to problems such as control is difficult. Researchers at the Alternative Energy Study Center of LPPM, UPN Veteran east of Java have developed a continuous pilot process, consisting of a reactor and various downstream separation steps, to produce biodiesel of a saleable quality (fig.1).

Based on these problems it is necessary to look for a new process which is not so complicated, and needs shorter time. Recent researches have indicated that oscillatory flow in a baffled tube has significant potential for process and product enhancement in a wide range of application. Stonestreet and Harvey (2005) reported that oscillatory flow reactor is a novel type of continuous reactor, in which tubes fitted with orifice plate baffles have an oscillatory motion superimposed upon the net flow of the process fluid. These improvements and diversification of feedstock can decrease the price of biodiesel, making it a more realistic competitor to petrodiesel. This paper shows that it is feasible to perform this reaction in an oscillatory reactor at a lower residence time. The reaction was performed in a laboratory scale, using crude fish oil and technical grade methanol as the feedstocks, and NaOH as the catalyst. Following this, the design parameters shall be applied in fabricating the Oscillatory Reactor for pilot plant scale fatty acid methyl esters production.

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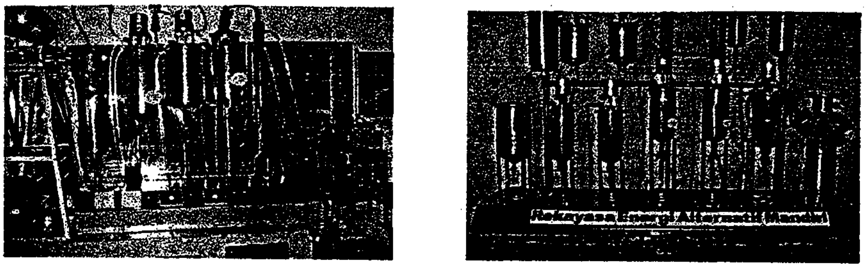

Figure 1. Experimental biodiesel plant

THEORI

Chemically, biodiesel is called fatty acid methyl ester if the alcohol used is methanol. The three basic methods of ester production from oils are 1) base catalyzed transesterification, 2) acid catalyzed esterification, and 3) enzymatic catalysis. Each reaction has associated optimal operating parameters and conversion, although much of the available literature emphasizes the base catalyzed route because it is claimed to be the most economical. The resulting reaction is called transesterification where the catalyst speeds the exchange of glycerol with three methanols creating methyl esters of fatty acids as noted in equation 1.

$$\begin{array}{lcl} H_2C-O-COR_1 & & H_2C-OH \\ HC-O-COR_1 + 3\,CH_3OH & \underset{\longleftarrow}{\xrightarrow{\text{katalis}}} & HC-OH \;+3\,(R_1COOCH_3) \quad (1) \\ H_2C-O-COR_1 & & H_2C-OH \end{array}$$

Triglycerides Methanol Glyserol Methyl Esters

The reaction progresses in three reversible steps: 1) the triglyceride [TG] reacts with the methanol [A] to form a diglyceride [DG] and a fatty acid ester [E], 2) the diglyceride reacts with the methanol [A] to form a monoglyceride [MG] and a fatty acid ester [E], and 3) the monoglyceride reacts with the methanol [A] form glycerin [GL] and a fatty acid ester [E]. The stepwise reactions are;

$$TG + A \rightleftarrows DG + E \qquad (2),$$
$$DG + A \rightleftarrows MG + E \qquad (3),$$
$$MG + A \rightleftarrows GL + E \qquad (4),$$

The general form of the governing set of differential equations characterizing the stepwise reactions involved in the transesterification TG is in equation;

$$\{d[TG]/dt\} = -k1[A][TG] + k2[E][DG] \qquad (5)$$
$$\{d[DG]/dt\} = k1[A][TG] - k2[E][DG] - k3[DG][A] + k4[E][MG] \qquad (6)$$
$$\{d[MG]/dt = k3[A][DG] - k4[E][MG] - k3[MG][A] + k4[E][GL] \qquad (7)$$
$$\{d[GL]/dt\} = k5[A][MG] + k6[E][GL] \qquad (8)$$
$$\{d[E]/dt\} = k1[A][TG] - k2[E][DG] + k3[A][DG] + k4[E][MG] + k5[MG][A] - k6[E][GL] \qquad (9)$$
$$\{d[A]/dt\} = -\{d[E]/dt\} \qquad (10)$$

Because the overall reaction rate equation are very complicated in the form of simultaneous differential equations, the solutions can only be achieved numerically to calculate A, E, TG, DG, MG, and GL.

MATERIAS AND METHODS

Pretreatment as optional process steps are only quite if the feedstock quality does not meet the following specification; FFA content (max. 0.2%), and water content (max.0.1%). The fatty acid profile of

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crude fish oil was analyzed using the GC method and is listed in table 1. Methanol and sodium hydroxide were from REAM chemical reagents.

Table 1. Fatty acid profile of fish oil used in this research.

Fatty Acids	Composition (%wt)
Palmitic	6.8
Stearic	5.8
Oleic	50.3
Linoleic	11.4
Linolenic	15.5
Erucic	10.2

A laboratory-scale oscillatory reactor (fig. 2a) was developed and tested on overall process parameters. This reactor column had an inner diameter of 50mm, and a distance of 75 mm between baffles. The nominal liquid hold-up on each baffle was 140 ml, totaling 2800 ml of the column. The reactor consisted of a vertically tubes of 1,500 mm length. The lower end of the column was fitted to a 5000 ml bottom flask as the re-boiler. A water-cooled multi tube condenser was fitted to the top of the column to recover alcohol which was combined with reactants and pumped back into the column. The feeds were pumped from the feed vessels using a gear pump. Temperatures were maintained in the feed vessels and supply lines by electric temperature controllers, regulating the outputs to the coil heater beneath the feed vessels. The flow sheet is shown in fig-2b. The molar ratio of methanol to crude fish oil used was maintained at 5:1. It was necessary to use an excess of methanol to move the equilibrium of the reaction to the product side. Solid 99.2% pure NaOH (32.4g) was dissolved in each liter of the 99.9% pure methanol feed.The NaOH was mixed with the methanol before each experiment for at least 1h at 40°C in the feed vessel. The product mixture was withdrawn from the re-boiler to a glycerol-ester separator. The glycerol-ester separation was operated by gravity in a decanter with an adjustable entry point. After the process took place for about 15 minutes, samples were taken and analyzed for its ester numbers. These activities were repeated every 15 minutes, until the ester numbers content of the samples were constant. This indicated that steady state condition had been reached. Then the products were analyzed to determine their viscosity, density, pH and the volume fraction of glycerol, but these measurements were not sufficient to determine the quality of the biodiesel. Hence, the samples were sent to a commercial laboratory for ester numbers, acid numbers, flash point, cloud point, pour point, and heating value analysis. Before all analyses the product was allowed to settle overnight. The main parameters of interest in this initial series of experimental runs were

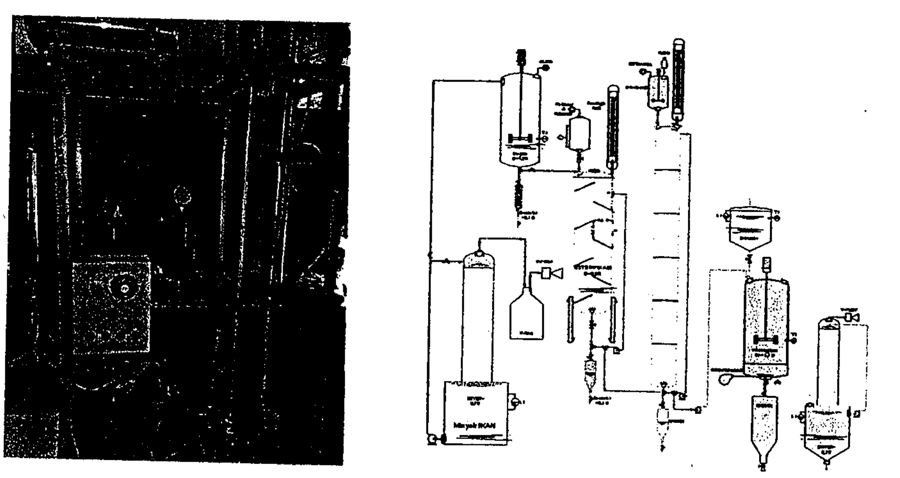

Figure 2. Illustration of oscillatory lab-scale reactor system and flow sheet.

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the temperature and residence time. These were varied within the ranges 30–70°C and 5–30min respectively. All other variables such as molar ratio and amount of catalyst were kept constant.

RESULTS AND DISCUSSION

The experimental data were collected after the process reached steady state. For all variables studied, the triglyceride conversation, x increased with time because more chances were available for the reactants to collide with each others. The reaction period t depended upon the crude fish oil flow (F_{TG}) and methoxide flow rates (F_A) as presented equation:

$$t = (2055.72\,(F_{TG})^{-0.1642}) / (F_A) \qquad (11)$$

Decreasing of crude fish oil flow rate from 5 to 1 cm^3/minute raised the value of conversion. The triglyceride conversions also increased, if methanol to crude fish oil ratio and temperature were raised from 3:1 to 7:1 and from 30° to 65°C. The increase in methyl ester concentration was followed by an increase in glycerol concentration as it was liberated from triglyceride molecules. However, the relative proportion of glycerol produced was not always the same as that of the esters produced. This is due to intermediate products such as diglyceride and monoglyceride. Triglyceride concentration decreased as the reaction proceeded; after 12 min, triglyceride concentration was only 5.8%. The effect of temperature on crude fish oil trans-esterification was studied at a sodium hydroxide catalyst concentration of 1 % and a methanol/oil molar ratio of 5:1. The minimum temperature used in this work was 30°C. The maximum temperature studied was 65° C because the boiling point of methanol is 68° C. At 50° C, conversion of triglyceride to monoglyceride was 70.7% as compared to 91.82% conversion at 65° C. The best kinetic was a pseudo second-order model for the initial stages of the reaction, followed by first-order kinetics. of magnitude of k is $k_{MG} > k_{DG} > k_{TG}$. These data were used to determine the Arrhenius energy of activation from a plot of the reaction rate constant *(k)* *vs.* the absolute temperature *(T)*, according to the equation:

$$k_{MG} = 9.533210^3\ {}_e - 8342.4/(RT) \qquad (12)$$

$$k_{DG} = 7.441310^3\ {}_e - 1698.3/(RT) \qquad (13)$$

$$k_{TG} = 8.687510^3\ {}_e - 1846.6/(RT) \qquad (14)$$

where Ea is the energy of activation, and R is the gas constant. At the lowest catalyst concentration (0.1%) there was a lag, in monoglyceride production, followed by a rapid increase in rate after 2 min. The highest conversion was 94.2% ester numbers was 251.4, and this was obtained at process conditions of 12 minutes, methanol to oil ratio of 5:1, temperature of 60°C, and catalyst concentration of 1.2%.

CONCLUSION

From the results and discussion, the following conclusion could be presented.

a. the overall rate of reaction was controlled by chemical reaction. Chemical reaction constant was affected by reactant ratio, and catalyst concentration of the system logarithmically and exponentially by temperature.

b. From all variables studied, it seemed that temperature, feeding methanol to crude fish oil ratio, and reaction time had the highest effect on the triglycerides conversion, so these variables are controlling parameters in designing a vertical tube reactor provided with oscillatory flow. Other criteria employed to take into account are the effect of baffles and rate of reaction. Geometric configuration is achieved by maintaining the baffle spacing to diameter ratio and fractional open area of the baffle.

c. Total residence time in the oscillatory reactor was 8-15 minutes, which is 6 times shorter than in typical batch processes. The productivity of the oscillatory reactor system is about 5 times biodiesel volume per reactor volume per hour. The highest triglycerides conversion in this research was 94.2%, and this was obtained at residence time of 12 minutes, temperature of 60°C, and methanol to oil ratio of 5:1 (molar).

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